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THE DESCLOIZITE-MOTTRAMITE SERIES OF VANADATES FROM MINAS DO LUECA, ANGOLA

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ABSTRACT

The results are given of a chemical, microchemical and *x*-ray investigation of vanadium minerals from a new locality in West Africa—Minas do Lueca in Angola, together with comparative data for similar minerals from other localities. A rapid and simple technique of microchemical analysis has been devised which enables accurate discrimination to be made between different members of the descloizite $(Zn)Pb(VO_4)OH$–mottramite $(Cu)Pb(VO_4)OH$ isomorphous series. A description is given of the mode of occurrence and origin of the vanadium minerals at the Lueca Mine, and of the associated tarbuttite Zn_2PO_4OH and volborthite $Cu_3(VO_4)_2\cdot 3H_2O$.

INTRODUCTION

In the course of a study of a new vanadium deposit at Minas do Lueca in Angola, Portuguese West Africa, it was found that there was a wide variation in color and physical properties of the "descloizite"-type minerals occurring in the deposit. Reference to literature showed that there is still some confusion in the nomenclature of these minerals and that the *x*-ray powder diffraction data have not been fully established for a representative number of members of the isomorphous series to which these vanadates belong. For paragenesis studies of the vanadium mineralization at Lueca, it was found necessary to make precise identification of members of the series present in the ore. For this purpose, complete chemical analysis was found to be too tedious in view of the large number of specimens involved, and *x*-ray powder photography too indefinite; consequently a rapid microchemical technique has been devised which enables precise discrimination to be made between members of the descloizite-mottramite series.

CHEMICAL COMPOSITION OF THE DESCLOIZITE GROUP

The "descloizite"-type minerals may be expressed by the formula $(Zn,Cu)Pb(VO_4)OH$, and a complete isomorphous series exists between the zinc and copper end-members—descloizite and mottramite respectively. The combined content of ZnO and CuO approximates 20% throughout the series, and it has been proposed that descloizite should refer to that half of the series in which the ZnO content exceeds 10%, and mottramite to the other half of the series in which the CuO content is greater than 10%. The chemical analyses of six members of the series are given in Table 1. It is suggested that members with more than 18% ZnO should be referred to as *descloizite,* those with between 10 and 18%

ZnO as *cuprian descloizite*, those with between 2 and 10% ZnO as *zincian mottramite*, and those with less than 2% ZnO as *mottramite*. Minor amounts of manganese and iron are known to substitute for (Zn,Cu), and arsenic, phosphorus and molybdenum substitute for vanadium.

TABLE 1. CHEMICAL ANALYSES OF DESCLOIZITE AND MOTTRAMITE

	A*	B*	C*	D	E*	F
PbO	54.9	54.8	51.9	54.5	54.0	54.56
ZnO	19.18	15.22	10.65	5.12	3.61	2.62
CuO	0.83	4.62	8.83	13.9	15.45	16.84
V_2O_5	21.07	22.27	17.38	22.65	20.38	22.73
As_2O_5	n.d.	n.d.	trace	n.d.	n.d.	n.d.

* New analyses.

n.d. = not detected or reported.

A. *Descloizite*, Broken Hill, N. Rhodesia. Coarsely crystalline aggregate; dark-brown colour, yellowish-beige streak.

B. *Cuprian descloizite*, Oliphantsfontein, South-West Africa. Large, dark greenish-black crystals, pale lime-yellow streak.

C. *Cuprian descloizite*, Minas do Lueca, Angola. Greenish-black coarse crystal aggregates, pale brownish-yellow streak.

D. *Zincian mottramite*, Nagreib, Otavi, South-West Africa. Olive-green botryoidal, fibrous mass; olive-green streak. Bannister and Hey (1933).

E. *Zincian mottramite*, Oliphantsfontein, South-West Africa. Velvety surfaces, drusy aggregates; deep lime-green streak.

F. *Mottramite* (near end-member), Uris Mine, Tsumeb, South-West Africa. Grass-green crystals; bright green streak.

X-RAY INVESTIGATION

The published *x*-ray powder data for the descloizite series are incomplete. The first attempt to clarify the nomenclature was by Bannister and Hey (1933) and they concluded that the powder data for descloizite, cupro-descloizite, psittacinite, mottramite, chilëite, eusynchite and dechenite were identical and that they could all be expressed by the formula $(Zn,Cu)Pb(VO_4)OH$. This conclusion was modified recently by Kingsbury and Hartley (1956) who showed that although the spacings for descloizite and mottramite are similar above 1.652 Å, there were significant differences in smaller spacings. Guillemin (1956) has also shown this to be the case for the pure synthetic end-members; Guillemin has synthesized two forms of mottramite of different structure and cell-size, and has proposed the terminology of α-mottramite and β-mottramite, the β-form having slight excess of adsorbed water. He has found that naturally occurring mottramite has the α-type structure. In Table 2, new

TABLE 2. X-RAY POWDER DATA FOR THE DESCLOIZITE-MOTTRAMITE SERIES: 9 CM. CAMERA, CoKα, λ=1.7889 Å, CORRECTED FOR FILM SHRINKAGE (NOS. 2, 3, 4 AND 5); CuKα, λ=1.537 Å (NOS. 1 AND 6, GUILLEMIN 1956)

1. Synthetic descloizite (Guillemin, 1956).
2. Descloizite, Broken Hill, N. Rhodesia (Anal. A, Tab. 1), (Fig. 1).
3. Cuprian descloizite, Oliphantsfontein, S.W. Africa (Anal. B, Tab. 1).
4. Cuprian descloizite, Minas do Lueca, Angola (Anal. C, Tab. 1).
5. Zincian mottramite, Oliphantsfontein, S.W. Africa (Anal. E, Tab. 1), (Fig. 1).
6. Synthetic α-mottramite (Guillemin, 1956).

	d Å					
	1	2	3	4	5	6
1	5.08 m	5.03 M	5.02 M	4.96 M	4.99 W	5.04 mF
2	4.68 ff	4.68 VW	4.64 VW	4.58 VW	— —	4.61 ff
3	— —	— —	— —	— —	4.47 VW	4.39 ff
4	4.22 f	4.19 W	4.19 W	4.15 W	4.16 W	4.22 fm
5	4.02 ff	3.97 VW	3.96 VW	3.92 VW	3.94 VW	3.94 f
6	3.56 ff	— —	— —	— —	— —	3.57 fm
7	— —	3.49 W	3.50 W	3.47 W	3.50 W	3.53 ff
8	3.46 ff	— —	— —	— —	— —	3.45 f
9	— —	3.31 VW	3.30 VW	3.28 VW	3.28 VW	3.29 ff
10	3.21 F	3.20 S	3.19 S	3.13 S	3.19 S	3.22 F
11	— —	— —	— —	— —	— —	3.05 ff
12	3.01 ff	3.02 W	3.01 W	2.98 W	2.98 W	3.01 f
13	2.90 m	2.93 VW	2.96 VW	2.92 VW	— —	— —
14	— —	2.87 S	2.88 S	2.86 S	2.84 S	2.84 m
15	— —	2.68 M	2.69 M	2.66 M	2.65 M	2.68 f
16	2.64 m	2.64 M	2.65 M	2.63 M	2.63 M	2.64 f
17	— —	2.59 S	2.60 S	2.58 S	2.56 M	2.57 fm
18	2.54 ff	2.54 W	2.54 W	2.51 W	2.52 W	2.51 ff
19	— —	2.46 VW	2.45 VW	2.43 VW	2.45 VW	2.47 ff
20	— —	2.42 VW	2.41 VW	2.38 VW	— —	— —
21	2.30 m	2.29 M	2.29 M	2.27 M	2.28 M	2.29 ff
22	— —	2.22 W	2.22 VW	2.21 W	2.21 W	— —
23	2.10 fm	2.09 M	2.09 M	2.08 M	2.08 W	— —
24	1.96 ff	1.962 VW	1.961 VW	1.950 VW	1.952 VW	— —
25	1.88 f	1.897 VW	1.893 VW	1.885 W	1.899 VW	— —
26	— —	1.864 W	1.864 W	1.853 W	1.863 W	— —
27	1.77 f	1.777 M	1.772 W	1.767 W	1.780 W	— —
28	— —	1.750 W	1.754 VW	1.747 W	1.762 W	— —
29	1.65 f	1.647 VS	1.647 S	1.637 VS	1.642 S	— —
30	1.61 ff	1.604 M	1.604 M	1.598 M	1.609 M	— —
31	1.57 ff	1.564 S	1.560 M	1.551 M	— —	— —
32	— —	— —	— —	— —	1.538 M	— —
33	1.51 ff	1.512 W	1.508 W	1.499 W	1.504 W	— —

Lines below last spacing listed are too weak or diffuse for measurement. For Nos. 2, 3, 4 and 5, VS=very strong, S=strong, M=moderate, W=weak, VW=very weak.

TABLE 2 (*continued*)

	d Å					
	1	2	3	4	5	6
34	— —	1.496 W	1.495 W	— —	1.494 W	— —
35	— —	— —	— —	— —	1.451 W	— —
36	1.41 ff	1.409 S	1.410 M	1.400 M	1.405 W	— —
37	— —	1.393 VW	1.393 VW	1.381 VW	1.388 W	— —
38	— —	1.367 VW	1.371 VW	1.362 VW	— —	— —
39	— —	1.353 W	1.356 W	— —	— —	— —
40	— —	1.341 W	1.344 W	1.345 W	— —	— —
41	— —	1.332 W	1.334 W	1.329 M	1.335 M	— —
42	— —	1.246 VW	1.249 VW	— —	1.247 M	— —
43	— —	1.236 VW	1.241 VW	— —	— —	— —
44	— —	1.210 VW	1.210 VW	— —	— —	— —
45	— —	1.198 VW	1.200 VW	— —	— —	— —
46	— —	1.177 VW	1.179 VW	— —	— —	— —
47	— —	1.160 VW	1.161 VW	— —	— —	— —
48	— —	1.149 VW	1.144 VW	— —	— —	— —
49	— —	1.133 VW	1.132 VW	— —	— —	— —
50	— —	1.124 VW	1.123 VW	— —	— —	— —
51	— —	1.106 VW	1.106 VW	— —	— —	— —
52	— —	1.098 VW	1.097 VW	— —	— —	— —

x-ray powder data have been listed for four members of the series (nos. 2–5), the chemical analyses of which appear in Table 1(A, B, C and E); for comparative purposes, Guillemin's data are also listed for the pure synthetic end-members although he has not reported lines below 1.41 Å in the case of descloizite, and 2.29 Å in the case of α-mottramite. There is close agreement in the spacings and relative line intensities between 5.0 Å and 1.86 Å (lines 1–26) but substantial differences occur in the lower spacings, especially between 1.60 Å and 1.50 Å (lines 30–34), 1.41 Å and 1.33 Å (lines 36–41), and 1.25 Å to 1.09 Å (lines 42–52). The mottramite half of the series appears to have considerably fewer reflections at spacings lower than 1.38 Å (line 37). Some of these differences may be discerned in Fig. 1 which shows the powder photographs of descloizite and zincian mottramite.

MICROCHEMICAL TECHNIQUE FOR DETERMINATION OF MEMBERS OF THE DESCLOIZITE GROUP

One of the most useful qualitative microchemical reagents for the identification of several ore metals is potassium mercuric thiocyanate. Details of the procedure for the preparation of this reagent are given by

Short (1948), and the characteristics of the microchemical reaction products by both Short (1948) and Guillemin (1953) for zinc, cadmium, copper, cobalt, nickel, iron and other elements. With zinc and copper the reagent forms mixed crystals, and it occurred to the writer that this might provide an elegant method for the precise identification of this group of zinc-copper vanadates in view of the speed and simplicity with which the test can be performed.

The procedure for carrying out the microchemical analysis is as follows. About 5–10 mg. of the "descloizite" sample to be tested are positioned centrally on a 3″×1″ glass slide, and one drop of 1:1 nitric acid added from a capillary. The slide is then warmed gently over a spirit-lamp or micro-burner flame to dissolve the mineral and evaporate the nitrate solution to dryness. A characteristic blood-red precipitate of vanadic oxides is produced. A drop of 1:7 nitric acid is then added with a clean capillary to the assay to take the zinc and/or copper salts into solution, and the drop is then transferred by means of a capillary to another clean glass slide. A drop of the 3% aqueous solution of potassium mercuric thiocyanate confirmatory reagent is then placed on this slide adjacent to the test drop, and the two are merged by means of a platinum wire. After about half a minute, the double-salt thiocyanate reaction products appear, and the slide is then examined under a petrological microscope and their characteristics recorded.

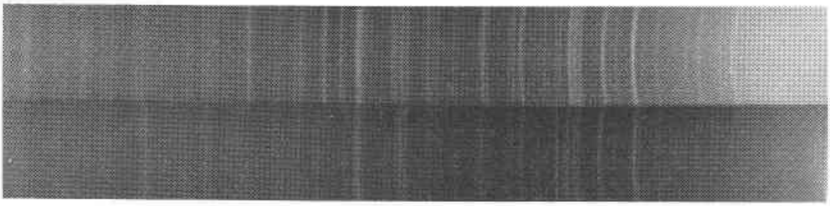

FIG. 1. *X*-ray powder photographs: CoK radiation, $\lambda = 1.7889$ Å; camera radius 9 cm. Above: Descloizite, Broken Hill, N. Rhodesia. ZnO:CuO = 19.18:0.83 (Analysis 2, Table 1). Below: Zincian mottramite, Oliphantsfontein, S.W. Africa. ZnO:CuO = 3.61:15.45 (Analysis 5, Table 1). For spacings in Å, see Table 2.

In the presence of zinc and absence of copper, a 3% solution of the thiocyanate reagent, $K_2Hg(CNS)_4$, in water, yields pure white feathery crystals; with copper and no zinc, green mossy clumps of fine acicular crystals. With varying amounts of copper and zinc together, a variety of mixed crystals are formed. As shown in Table 3, the descloizite members of the series yield white to purple feathery or simple crosses (for zinc) with no or few green crystals (for copper). The mottramite group give characteristic green mossy clumps of crystals (for copper) with no or very few dark violet crosses (for zinc). The only element which is sometimes present in the descloizite group of minerals and which interferes with this reaction is iron. Iron also yields purple to black crosses or feathery crystals with zinc, but however reveals its presence by tinting the solution a pinkish brown as well. If therefore the solution does not take on this color after addition of the thiocyanate, it may be deduced that interference due to the presence of iron is negligible.

MODE OF OCCURRENCE OF THE MINAS DO LUECA VANADIUM DEPOSIT

The vanadium mineral deposits at Lueca are located in the upper parts of a range of hills, striking in a north-south direction which rise up to 70 m. above the level of the Lucunga peneplane in Northern Angola. To the south this range of hills, which is only about 500 m. in width, falls gradually to the level of the peneplane, but to the north the slopes drop sharply to the banks of the Lueca river. The main Damba Plateau is separated from the Lueca hills by a narrow valley.

TABLE 3. ZINC AND COPPER MICROCHEMICAL REACTION PRODUCTS WITH POTASSIUM MERCURIC THIOCYANATE

Percentage ZnO in descloizite-mottramite series ($ZnO+CuO=c.20\%$)	Microscopic characteristics of thiocyanate mixed-crystal reaction products
Descloizite 20–18	Feathery crosses, white to mauve.
Cuprian descloizite 18–14	Simple crosses only, violet to black.
Cuprian descloizite 14–10	Simple crosses only, violet to black.
Zincian mottramite 10–7	Green mossy aggregates and simple violet crosses.
Zincian mottramite 7–3	Green mossy aggregates and fewer violet crosses.
Zincian mottramite 3–2	Dominant green mossy aggregates and rare violet crosses.
Mottramite 2–0	Green mossy aggregates and acicular crystals only.

The chief sedimentary formations of the area are believed to be Pre-Cambrian in age, and belong to the "Schisto-Gréseux" and "Schisto-Calcaire" systems. The former consist of Inkisi felspathic quartzites and sandstones, overlying Pioka red and grey sandstones, shales and basal conglomerate breccia. The older "Schisto-Calcaire" group is composed of a variable series of impure limestones, containing occasional algal fossils. The Damba Plateau and western flanks of the Lueca hills are composed of this limestone series; at Lueca the limestones dip 10–15° to the east, and the eastern flanks of the hills are made up of "Schisto-Gréseux" sandstones and quartzites dipping 20–50° to the west, the two series being separated by a presumed north-south fault along the axis of the Lueca range.

The surface of the Lueca hills is composed of argillaceous and siliceous eluvium, with a maximum thickness of about 5 m., consisting of numerous hematite boulders and fragments of siliceous rocks with sporadic vanadium minerals and manganese oxides. The soil is reddish brown containing grains of pisolitic laterite and small fragments of quartz. Below this eluvial cover, the rocks are intensely altered and fragmented; pipe structures are common and contain collapse breccias of silicified rocks with argillaceous and ferruginous earths and vugs lined with chalcedonic silica, descloizite, mottramite, vanadinite and other rarer minerals.

Mineralogy of the Vanadium Ores

Primary hypogene minerals are extremely rare at Lueca, and only traces of pyrite relics were found in limonite boxworks, together with a few grains of strongly fluorescent sphalerite, the latter being very similar to the sphalerite occurring in the Tsumeb Mine in South-West Africa.

Of the secondary supergene minerals, hematite is the most common occurring in the form of ochres in solution cavities, finely dispersed material in hematitized and silicified limestones, and as large masses showing prominent colloform banding. Considerable amounts of limonite are also present. Quartz is widespread in its distribution in the ore zone, and occurs as (*a*) cross-cutting veins and lenses of crustified and comb-structured white and green quartz, (*b*) replacement disseminations of microcrystalline euhedral clear quartz in silicified limestones (see Fig. 2,A), and (*c*) vug and solution cavity fillings of colorless euhedral crystals and chalcedonic gel silica. The silica of type (*c*) occasionally contains radiating spherulites of secondary copper silicates; these are azure to sky-blue in color, with a maximum size of about 2 mm. Three different *x*-ray powder patterns have been obtained for these silicates, and none agrees with the powder patterns for planchéite, shattuckite or chrysocolla from the Tantara Prospect, near Katanga, Belgian Congo. Other rare supergene minerals have been confirmed by *x*-ray powder photography.

Tarbuttite, Zn_2PO_4OH, occurs as saddle-shaped radial aggregates of pale green crystals, up to 3 cm. across, encrusting surfaces of hematite. The presence of zinc, phosphorus and arsenic has been confirmed by microchemical and spectrographic analysis. The following optical properties were determined: $\alpha=1.659$, $\beta=1.685$, $\gamma=1.702$ (for Na light, $\pm.003$), optically $(-)$, $2V=50°$. The presence of arsenic in addition to phosphorus suggests the possibility that an isomorphous series may exist between tarbuttite and the new triclinic zinc arsenate, paradamite Zn_2AsO_4OH, described recently by Switzer (1956). *Volborthite*, $Cu_3(VO_4)_2 \cdot 3H_2O$, has also been identified, and the *x*-ray powder data agree closely with those reported recently by Guillemin (1956). It occurs as bright to olive yellow micaceous brittle flakes, up to 1 cm. across, with high lustre and perfect cleavage. The refractive indices are >2 and <2.09 with no pleochroism; it shows high dispersion and twinning is also characteristic. The volborthite occurs as an alteration product on the surfaces of descloizite and mottramite crystals, and also as crystals lining the central cavities of geodes of green quartz.

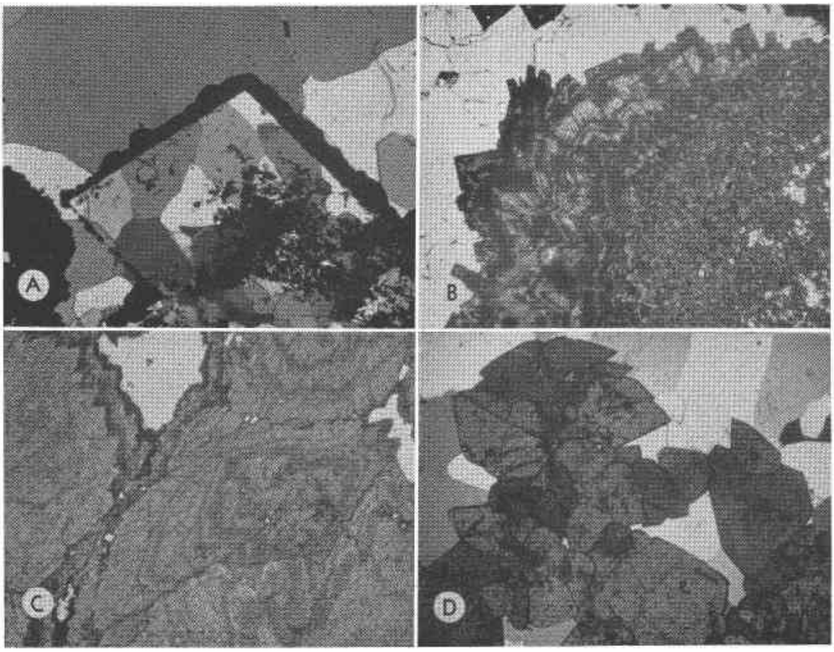

FIG. 2. Thin section photomicrographs of ore specimens from Minas do Lueca, Angola.

Upper left: Dolomite limestone totally silicified by supergene processes. Note the relic outline of original rhombic carbonate replaced by mosaic of silica, with overgrowth by colloform hematite and goethite. (Polarized light, ×55.)

Upper right: Small cavity filling of euhedral zoned mottramite and quartz. Note the diffuse boundary between the finer-grained disseminated mottramite in the wallrock and the cavity lining. (Ordinary light, yellow filter, ×20.)

Lower left: Prominent color zoning and pleochroism (red to yellow) in coarsely crystallized mottramite. Interstices rimmed with manganese oxides and goethite and filled with chalcedonic silica and opal. (Ordinary light, yellow filter, ×20.)

Lower right: Aggregate of euhedral mottramite crystals enclosed in a mosaic of secondary quartz. (Polarized light, yellow filter, ×20.)

Descloizite, $(Zn,Cu)Pb(VO_4)OH$ *and mottramite,* $(Cu,Zn)Pb(VO_4)OH$

The microchemical method of analysis has shown that at Lueca mottramite members of the series are far more common than the descloizites.

The composition has been found to vary substantially and the following four main types have been discriminated:

1. Cuprian descloizite, intermediate member, CuO:ZnO 1:5
2. Zincian mottramite, intermediate member, CuO:ZnO 2:1
3. Zincian mottramite, intermediate member, CuO:ZnO 5:1
4. Mottramite, near end-member, CuO:ZnO 10:1

Other intermediate members have also been recognized (e.g. analysis C, Table 1), but do not constitute significant amounts of the ore. Qualitative spectrographic analysis has shown the presence of substantial amounts of As, Cr and Mn, and traces of Fe, Mo, Ni, Ag, Sn, Ti and P. The Cr, As, Mo, and P are probably substituting for vanadium, and the Fe and Mn for (Cu,Zn).

The descloizite at Lueca is usually dark reddish brown in color, whereas the mottramite is more inclined to a dark blackish green or more rarely a pistachio green. Both occur as crystalline sheaf-like aggregates, often with a fibrous structure and with color banding normal to the length of the fibers. Well-formed euhedral crystals (see Fig. 2,D) also occur in vugs associated with quartz, chalcedony and rare vanadinite. Very large amounts of both descloizite and mottramite however occur as minute anhedral replacement grains in the silicified limestone wallrocks (see Fig. 2,B); occasional spherulites up to 1 mm. in size are also found on the walls of joints in massive hematite. Rhythmic banding of red, yellow and green zones is conspicuous in thin-sections (Fig. 2,B and C). Relics of vanadinite crystals partially replaced by descloizite and mottramite are common, although vanadinite in places overgrows the other vanadates. Green quartz is common in the vanadium ore zone, and the green color has been found to be due to the presence of myriads of minute prisms and acicular aggregates of the descloizite-mottramite group; the size of these crystal inclusions reaches a maximum of about 15×250 microns, but most are considerably smaller than this.

Vanadinite, $Pb_5(VO_4)_3Cl$

This mineral is much less common than the other vanadates with which it is intergrown. It occurs as small orange-brown prismatic crystals up to 3 mm. in diameter, and as fine straw-like crystals and tufted fibers, pale yellow to orange in color. Deposition of the vanadinite overlaps with that of descloizite and mottramite.

ORIGIN OF THE VANADIUM ORE MINERALS

The occurrence of the vanadium minerals at the Lueca Mine shows general geological similarities with other vanadium deposits in South-West Africa. At Grootfontein and Abenab the more common type of deposit is usually associated with limestones and dolomites, and the ore minerals occur in vugs, interstices, collapse breccias in the form of pipes, and solution cavities, associated with considerable amounts of secondary calcite. In the Lueca area, however, the rocks are dominantly siliceous in nature and the vanadium-bearing minerals are associated with quartz and chalcedony, carbonate minerals being entirely absent. A comparable deposit is the one at Kazakstan in the Soviet Union where vein-like lenses of quartz with vanadium minerals occur at the contact of recrystallized limestones and sandstones. The Lueca-type deposit appears to be unusual in Africa.

Previous workers including Schwellnus (1946) and Taylor (1954) have concluded from spectrographic data that inadequate amounts of vanadium are present in primary sulphide minerals to account for its extensive concentration during the weathering and oxidation of base-metal deposits. However at Broken Hill, N. Rhodesia, Taylor (1954) has reported 0.0003–0.0005% V in the dolomite of the Broken Hill Series, as compared with 0.0117–0.0134% V in argillaceous members of the Series. Protracted weathering of such argillaceous rocks under tropical conditions, especially in arid regions, could account for adequate quantities of vanadium. The most likely source at Lueca is the Pioka Series containing red shales, which overlie the Schisto-Calcaire Dolomite, and which have been removed by erosion. Reprecipitation of the vanadium liberated by weathering may take place at the locus of lead, zinc and copper mineral deposits, but if the groundwaters are strongly acidic, as is frequently the case in proximity to oxidizing orebodies, the soluble lead-zinc-copper vanadates will migrate and be deposited under the optimum reducing conditions in a favorable rock or structure. It has been shown experimentally by Guillemin (1956) that mottramite is precipitated at pH 4 by the replacement of vanadinite by copper sulphate solution. He has also shown that volborthite is soluble in acid solution but will start to precipitate when the pH approaches 4.5; acid solutions will however precipitate volborthite on the surfaces of malachite and azurite, as in some Russian deposits, and in a barium or calcium rich environment, vesigneite $Cu_3Ba(VO_4)_2OH$ or tangeïte $CuCa(VO_4)(OH)$ respectively are formed.

The mineralogical assemblage at Lueca of contemporaneous descloizite-mottramite, volborthite, tarbuttite and planchéite-type copper silicates suggests therefore deposition in a moderately acidic environment together with extensive silicification of the limestone wallrocks. Some evidence is seen of the presence of rare primary sphalerite and pyrite, and the tectonic structure of the Lueca hills provided the channelway for the original deposition of the primary deposit of sulphides in the dolomitic limestone where it is faulted against the quartzites and sandstones. It is concluded that the Lueca vanadium deposit is of residual origin, and has been formed in the area of a pre-existing Cu-Pb-Zn orebody the vanadium being derived from weathered sediments; the presence of such abundant quartz, obviously deposited under exogenic conditions in view of its intimate association with vanadates, phosphates and copper silicates and the extent of the silicification of the dolomitic limestone is unusual, and may in part at least be due to a resurgence of low temperature "hydrothermal" solutions associated with renewed movement on the Lueca fault. Contamination of these ascending solutions was then brought about by the agency of near-surface groundwaters in the region of the oxidizing orebody.

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